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H$_3$PO$_4$ / oxide nanoparticles / polymer composites as proton conducting membranes

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ABSTRACT

Stable sols of 60 nm colloidal zirconia have been prepared by thermolysis of zirconium acetate. The surface complexing acetate groups have been replaced by phosphoric acid groups. Phosphate grafting has been characterized by dynamic light scattering, infrared spectroscopy, ^{31}P nuclear magnetic resonance and impedance spectroscopy measurements. These systems give acid and proton conductive particles (4.10^{-5} S.cm^{-1} at 70 % relative humidity).

H$_3$PO$_4$/ZrO$_2$/PVDF-*co*-HFP composite membranes have been synthesized. Impedance spectroscopy measurements allow discrimination between proton conduction at the surface of the phosphated particles and within free H$_3$PO$_4$ in the polymer. For the highest H$_3$PO$_4$/ZrO$_2$ ratios, the latter phenomenon prevails, giving a proton conductivity of 6.10^{-4} S.cm^{-1} at 70 % R.H.

INTRODUCTION

Proton-conductive membranes may find various applications in electrochromic devices, capacitors and fuel cells. This last application requires high proton conductivity, high chemical durability and a good stability against temperature and moisture modifications. Nafion®, a purely organic acid fluoropolymer used in such devices presents a swelling effect at high humidity and temperature but also a loss of proton conductivity at low water content [1]. Dispersions of H$_3$PO$_4$, H$_2$SO$_4$ or other acids in various polymers [2] may overcome this problem. However, stability of these systems towards hydrolysis can be poor. This leads to a loss of proton carriers during fuel cell running.

An interesting alternative is dispersion of high specific surface acid oxides. Indeed, they show both good proton mobility and their acid character is stable towards hydrolysis [3]. We here present a study relative to phosphate grafting onto polycrystalline nanometric sols of ZrO$_2$, and their use in H$_3$PO$_4$/ZrO$_2$/PVDF-*co*-HFP composite membranes.

EXPERIMENTAL

The zirconium acetate solution (Zr ~ 15-16% wt) and triethyl phosphate were purchased from Aldrich Chemicals. Acetic acid was purchased from SDS. PVDF-*co*-HFP (M$_w$ = 145000, HFP: 11% wt) has been friendly given by Atochem.

Dynamic light scattering (DLS) measurements were obtained on a Malvern 4700 photocorrelator. ^{31}P nuclear magnetic resonance was performed in a high-resolution liquid Bruker probe with a MSL 360 spectrometer. Impedance spectroscopy was performed with a HP4192A impedance analyzer. Silver electrodes were cast on the samples. Samples were equilibrated at 70 % relative humidity with a dilute sulfuric acid solution. X-ray powder diffraction was run with a Philips X Pert diffractometer at the CuKα wavelength. Infrared spectra were made with a Perkin Elmer 783 spectrometer on samples diluted in KBr powder.

Zirconia sol in water

Stable aqueous sols of crystalline zirconia were prepared as described by Matchett and al. [4] as follows: 20 ml of zirconium acetate were added to a mixture of 25 ml of glacial acetic acid and 19 ml of water. The clear solution was heated at 170°C for 3 hours in a pressure vessel. The residual zirconium acetate was eliminated by successive centrifugations and redispersions until the supernatant did not precipitate upon addition of H_3PO_4. The solid could be then dispersed again in 30 ml of water, giving a stable sol (ZrO_2 content: 55 g/l i.e. 0.45 mol/l).

H_3PO_4 grafted zirconia

To 30 ml of a ZrO_2 sol in water were added variable amounts of a 0.6 M aqueous solution of H_3PO_4. The mixture was stirred for 4 hours at room temperature. The solution was used as such for DLS and NMR measurements. For infrared spectra and impedance measurements, excess H_3PO_4 was eliminated by successive centrifugations and redispersions in water until the supernatant did not precipitate upon addition of zirconium acetate.

H_3PO_4/grafted zirconia/PVDF-*co*-HFP membranes

30 ml of triethylphosphate (TEP) were added to 30 ml of zirconia sol. Water and residual acetic acid were then evaporated under vacuum at 50°C, and the solution was completed to 35 ml with triethylphosphate and 1 ml of acetic acid, giving a stable sol in TEP.
Variable amounts of the solution were added to a PVDF-*co*-HFP solution (50 g/l in TEP). The mixture was stirred for 30 min and sonified during 1 h before addition of variable amounts of H_3PO_4 crystals dissolved in triethylphosphate. The solution was cast in PTFE Petri dishes and dried at 100°C during 24 h, giving 50 µm to 100 µm thick membranes.

RESULTS AND DISCUSSION

Zirconia sol characterization

X-Ray diffraction shows the sol to be monoclinic zirconia (figure 2). The crystalline domains determined from the width of the diffraction lines are around 5 nm. DLS measurements and TEM show the ZrO_2 particle hydrodynamic radius to be tightly distributed around 60 nm in the initial sol (table 1 and figure 1). Thus, the colloids observed in the solution are not primary particles, but aggregates of smaller domains. This has been also confirmed by transmission electron microscopy and X-Ray small angle scattering.
The perfect stability of the sol at pH < 5 is a first evidence for an electrostatic stabilization. The low particle size results from a strong complexation of zirconium by acetic acid that limits particle growth during synthesis.

Synthesis step	<Z> (nm)	Polydispersity
ZrO_2 sol in water after purification	62	0.04
ZrO_2 sol in TEP/acetic acid	64	0.06
H_3PO_4 grafted ZrO_2 (P/Zr = 1)	79	0.11

Table 1. Dynamic light scattering measurements on zirconia sols in various conditions

Infrared spectra of the dried ZrO_2 sol (figure 1a) exhibit characteristic absorptions of surface acetate species at 1550 cm^{-1} (C—O antisymmetric stretch), 1450 cm^{-1} (CH$_3$ deformation) and 1420 cm^{-1} (C—O symmetric stretch). The 130 cm^{-1} difference between symmetric and antisymmetric C—O stretching frequencies indicates that acetates are here bidentate bridging species [5].

Phosphate grafting

H_3PO_4 addition to the ZrO_2 sol causes an electrostatic destabilization; as a result, the hydrodynamic particle radius increases (table 1) and the solution precipitates within a few hours. Total elimination of the remaining free H_3PO_4 in the solution was checked by chemical analysis before recording infrared spectra. The acetate signature has nearly disappeared, while a strong absorption appears at 1050 cm^{-1} that is characteristic of PO_4^{3-} vibrations (figure 1b). The acetate species have been replaced by phosphates on the particle surface. The intensity of this absorption does not decrease after further rinsing in water, showing that phosphate bonding resists to hydrolysis.

The characteristic broad absorptions of the zirconium oxide network between 700 cm^{-1} and 400 cm^{-1} are still present after grafting. Furthermore, X-ray diffraction pattern are identical before and after grafting (figure 2). Therefore, we conclude that phosphates did not decompose the oxide particles during treatment to form bulk phosphates.
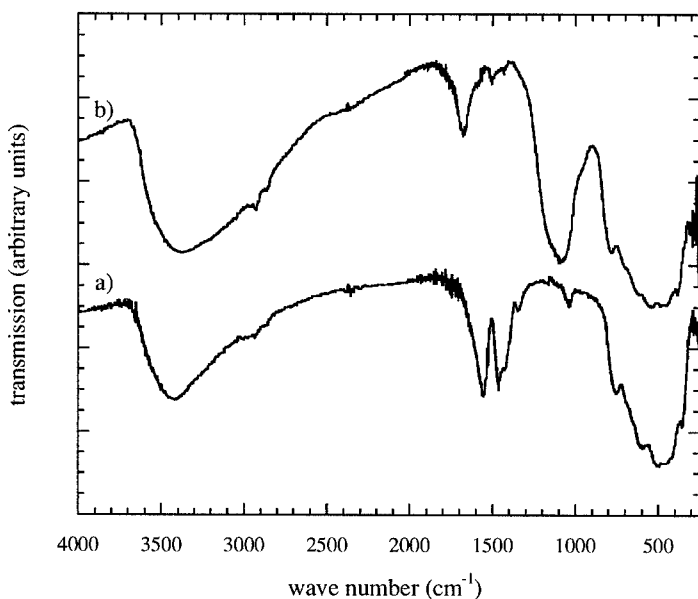

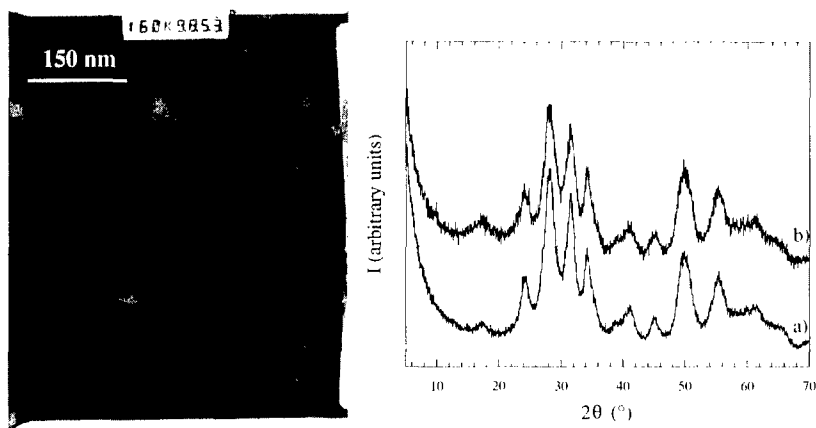**Figure 1.** Infrared spectra of a) ZrO$_2$ sol b) H$_3$PO$_4$ grafted ZrO$_2$ sol.

Figure 2. TEM of ZrO_2 particles and X-Ray powder diffraction of a) ZrO_2 particles b) H_3PO_4 grafted ZrO_2 particles

High resolution liquid state NMR ^{31}P spectra were performed on H_3PO_4/ZrO_2 mixtures with various P/Zr ratios (figure 3). For P/Zr ≤ 0.16, only a broad solid-like peak is observed, indicating that all the phosphates are bound to the zirconia particles. At a P/Zr = 0.31 ratio, free H_3PO_4 appears as shown by a sharp peak at 0.6 ppm.

Proton conductivity as measured by impedance spectroscopy on pressed powders of dried ZrO_2 sols is 10^{-8} S.cm^{-1}. After phosphate grafting, it reaches 4.10^{-5} S.cm^{-1}. This is a direct consequence of the increase in surface proton density and acidity.
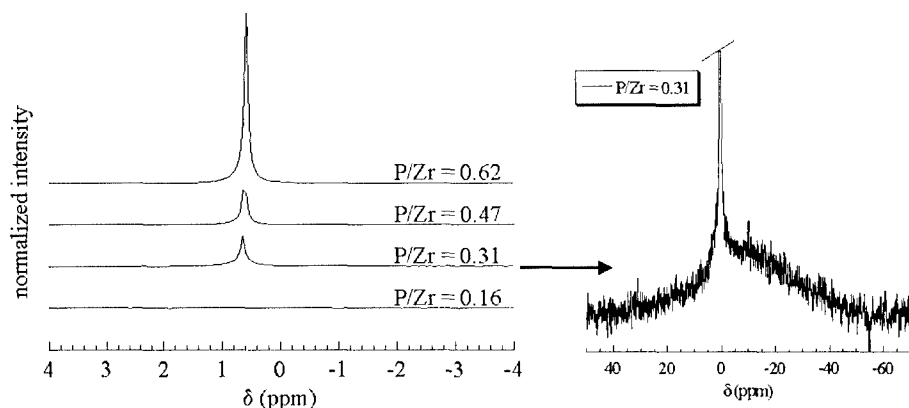

Figure 3. NMR ^{31}P spectra of H_3PO_4/ZrO_2 sol mixtures with variable P/Zr amounts. Chemical shifts reference: 85 % aqueous H_3PO_4.

H₃PO₄/ZrO₂/PVDF-*co*-HFP composite membranes

The proton conductivities of H_3PO_4/ZrO_2/PVDF-*co*-HFP membranes have been measured by impedance spectroscopy at a 70 % relative humidity. Various H_3PO_4/ZrO_2 ratios were investigated. The ZrO_2/PVDF-*co*-HFP weight ratio was maintained to unity (figure 4). We distinguish three different domains.

H_3PO_4/ZrO_2 molar ratios lower than 0.26: Impedance plots show only a slightly depressed semicircle. It is interpreted as proton conductivity at the surface of grafted zirconia. This conductivity increases with the H_3PO_4/ZrO_2 ratio. A higher surface coverage by acid phosphate groups offers a better proton diffusion pathway on the particle.

H_3PO_4/ZrO_2 ratios between 0.26 and 1.1: In addition to the low-frequency impedance of the blocking electrode, the impedance plots show two depressed semicircles with different resonance frequencies (figure 5a). This is characteristic of two impedances branched in series. The high-frequency conductivity continuously increases with the P/Zr ratio, while the low-frequency conductivity is merely constant at 3.10^{-7} S.cm^{-1}.

One of the semicircle is therefore attributed to proton conduction in free H_3PO_4 between the zirconia grains, the other one is due to conductivity on the phosphated particles. Indeed, according to the NMR results, liquid H_3PO_4 is present in these systems. To verify this hypothesis, some membranes have been thoroughly washed with water to remove the free H_3PO_4. The low frequency impedance drastically increases and a unique semicircle is observed again (figure 5b). Therefore, impedance spectra can be understood as surface conducting grains connected through free H_3PO_4 in the intergranular region.
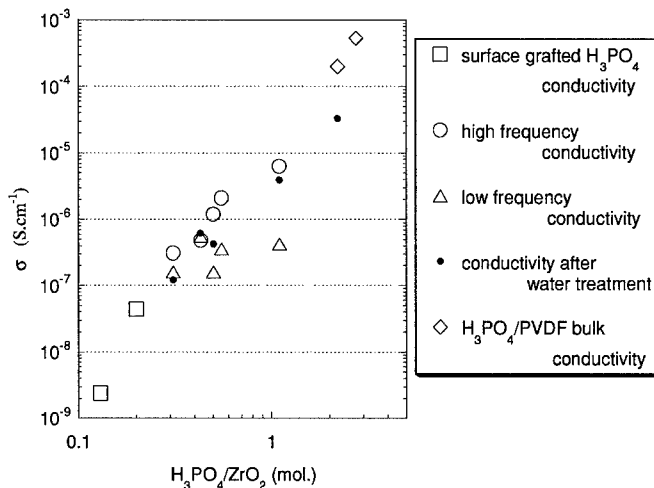

Figure 4. Protonic conductivities of H_3PO_4/ZrO_2/PVDF-co-HFP membranes as a function of H_3PO_4/ZrO_2 ratio at 70% relative humidity before and after water rinsing. ZrO_2/PVDF-co-HFP = 1 (wt).
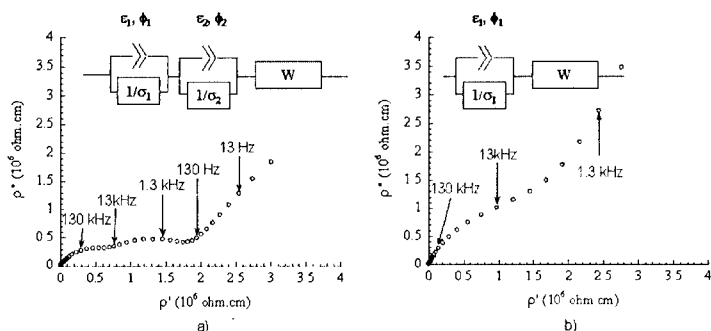
Figure 5. Cole-Cole diagrams and fitting circuits for $H_3PO_4/ZrO_2/PVDF$-co-HFP membranes ($ZrO_2/PVDF = 1$ (wt); $H_3PO_4/ZrO_2 = 0.55$ (mol)) **a)** before rinsing **b)** after rinsing. Frequencies are indicated. W = electrode impedance.

$\underline{H_3PO_4/ZrO_2 \text{ ratios above } 1.1}$: Impedance plots show a unique semicircle again. Conduction relative to free H_3PO_4 becomes predominant and short-circuits migration on grafted zirconia. The higher values of membrane protonic conductivity (6.10^{-4} S.cm^{-1}) are thus attributed the bulk diffusion of protons through free phosphate species in the PVDF matrix.

CONCLUSION

The acid functionalization of nanocrystalline ZrO_2 sols by H_3PO_4 gives proton conductive particles (4.10^{-5} S.cm^{-1}). Infrared study shows that complexing acetate surface groups are replaced by phosphate groups stable towards hydrolysis.

In the $H_3PO_4/ZrO_2/PVDF$-*co*-HFP composite membranes, proton conduction at the surface of phosphated particles or in the $H_3PO_4/PVDF$ matrix can be distinguished by impedance spectroscopy measurements. For higher H_3PO_4/ZrO_2 ratios, the latter phenomenon becomes predominant and short-circuits the others, giving membrane conductivities as high as 6.10^{-4} S.cm^{-1} at room temperature and 70 % relative humidity.

ACKNOWLEDGMENTS

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